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(54) **Marine/vegetable oil blend and products made therefrom.**

(57) The specification discloses a method for the preparation of a bland, keepable marine oil/vegetable oil which does not contain hydrogenated marine oil. The blend will retain its blandness for at least three months without development of a "fishy" odour and can be used for frying, baking or the preparation of edible compositions such as margarine. The result is achieved by blending the oils during or shortly after a refining process and overcomes the long-standing requirement that marine oils should be hydrogenated before use in edible compositions.

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spreads, salad dressings, sauces, gravies and other condiments as well as oil blends per se for use in frying and baking, including water and oil emulsion systems, whether separable, such as dressings, or not, such as spreads.

It is vital for the performance of the invention that substantially no deterioration of the marine oil occurs before blending. If such deterioration does occur, producing a "fishy" odour, then blending will only dilute this odour and not remove it. It is considered possible that blending prevents the formation of odour by limiting the oxidative degradation of the marine oil. To this end it has been noted that even in blends containing below 25% marine oil an odour eventually develops which is partially characteristic of "off" vegetable oil and quite unlike the characteristically nauseous and fetid odour of aged fish oil.

A particular advantage of the present invention is that the products contain many of the long-chain polyunsaturated fatty acids of dietary significance which are found in fish oil. Moreover, the possible long term storage of the products of the present invention enables inter-seasonal and inter-species blending of fish oils to compensate for the marked seasonal and special variation of fatty acid content, especially as is found with menhaden and herring oils.

Oil blends within the scope of the present invention are suitable for shallow frying and baking without exhibiting the development of a pronounced fishy odour. The preferred oil blends have 10% or less marine oil with respect to the total oil content.

Preferably, refining includes the step of treating the marine oil with silicate. More preferably, the silicate treatment comprises either a so-called "silicate boil" or silicate column refining. In general, the refining techniques employed herein are similar to those known in the art and described in Bailey, (cit. ultra). However, particular care should be taken that the oil is not subjected to conditions of high temperature which are believed to reduce the EPA and DHA content. More particularly, it is important that the temperature during, for example, deodorisation, should generally not exceed 200 °C. At higher temperatures some components of the oil may polymerise.

It is believed, as a result of UV absorption studies, that prolonged heating of unhydrogenated fish oils to temperatures above 200 °C, or even to slightly lower temperatures for extended periods, promotes the formation of a monomeric cis-cis-trans conjugated triene and a related dimeric diene. While the formation of these reactive species does not, at least initially, reduce the titre of EPA and DHA in the oil, the dietary significance of these compounds has not been fully investigated. Thus, methods of refining by high-temperature molecular distillation to remove "fish smell precursors" chemically modify the product such that reactive species of unknown physiological effect are present.

In order that the present invention may be understood further it will be illustrated by way of the following examples.

### EXAMPLE 1

#### PREPARATION OF COMPOSITION BY SILICA REFINING

Menhaden oil was extracted with methanol to reduce the free fatty acid content and neutralized with an excess of 0.1 N NaOH. The alkali-neutralized oil was bleached with 8% R169 bleaching earth at 90 °C for 45 minutes under vacuum.

After filtering off the earth, the oil was dissolved in two volumes of hexane and passed through a silica column with a volume such that the ratio of silica to oil was 1:2. The oil was eluted from the column with a further four volumes of hexane.

The hexane solvent was distilled off and the oil deodorized at 180 °C for 5 hours under N<sub>2</sub> at 3 mbars. 0.01% citric acid and 0.01% TBHQ were added at the beginning and the end of deodorization.

The oil was deodorized below 200 °C and the deodorized oil was blended immediately with vegetable oil.

### EXAMPLE 2

TABLE 1

| Oil/oil blend        | Odour    |           |             |            |
|----------------------|----------|-----------|-------------|------------|
|                      | + 24 hrs | + 2 weeks | + 4 weeks   | + 5 months |
| 10% menhaden in corn | bland    | bland     | bland       | bland*     |
| 25% menhaden in corn | bland    | bland     | bland       | -          |
| 50% menhaden in corn | bland    | bland     | slight fish | -          |
| 75% menhaden in corn | bland    | bland     | slight fish | -          |
| 100% menhaden        | off      | -         | -           | -          |

\* repeated successfully with 10% menhaden oil in sunflower oil and 10% menhaden oil in groundnut oil.

#### EXAMPLE 5

#### FRYING PROPERTIES

The 10% menhaden oil in corn oil was heated to 180 °C and used to fry frozen potato chips. Frying continued for about 20 minutes. Very few members of a taste panel reported a flavour of fish in the chips.

#### EXAMPLE 6

#### DRESSING PRODUCTS

Using fish oil and vegetable oil blends obtained by the method of Examples 1-3, edible compositions were prepared for use as salad dressings, and stored for periods of up to one year. Table 2 provides a formulation for one such composition.

TABLE 2

| Ingredient | %       |
|------------|---------|
| Oil Blend  | 43%     |
| Vinegar    | 18%     |
| Starch     | 6%      |
| Salt       | 4.8%    |
| Garlic     | 1%      |
| Onion      | 0.5%    |
| Flavour    | >1%     |
| Colour     | tr      |
| Water      | to 100% |

TABLE 5

| Sample | Oil Blend |          | Evaluation |                       |                        |
|--------|-----------|----------|------------|-----------------------|------------------------|
|        | Veg. Oil  | Fish Oil | Immediate  | 6 months<br>(ambient) | 12 months<br>(chilled) |
| A      | 100% bean | -        | acceptable | acceptable            | "old oil" flavour      |
| B      | 95% bean  | 5%       | acceptable | slight fish           | no fish                |
| C      | 90% bean  | 10%      | very fishy | unacceptable          | very bad               |

### Claims

1. A process for the preparation of a bland marine/vegetable oil blend which comprises blending unhydrogenated marine oil with vegetable oil during or shortly after refining of the marine oil, the ratio of marine oil to vegetable oil being less than one part of marine oil to three parts vegetable oil.

2. An edible composition comprising both bland unhydrogenated marine oil and vegetable oil in a ratio of not more than 1:3, which retains flavour stability, at ambient temperature, for at least three months.

3. The invention of either claim 1 or claim 2, wherein the marine oil is selected from the group comprising sardine oil, pilchard oil, menhaden oil, herring oil, anchovy oil, shark oil, cod oil and blends thereof.

4. The invention of either claim 1 or claim 2, wherein the vegetable oil is selected from the group comprising corn oil, sunflower oil, groundnut oil, olive oil, safflower oil, sesame oil, palm oil, cottonseed oil, soybean oil and rapeseed oil.

5. The invention of either claim 1 or claim 2, wherein the ratio of marine oil to vegetable oil is not more than 1:9.

6. A process according to claim 1, wherein refining includes the step of treating the marine oil with a silicate, so as to adsorb impurities present in the oil.

7. A process according to claim 1 or 6, wherein the temperature of the oil is generally held below 200 °C during the refining process.

8. An edible composition according to claim 2 and selected from the group comprising mayonnaise, margarine and other such spreads, salad dressing and cooking or frying oil.